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Lawrence Livermore National Laboratory
Waste Certification Program

Sampling and Analysis Plan for Encapsulated Uranium Turnings

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Contents

1. PROJECT DESCRIPTION

1.1 Waste Description

This sampling and analysis plan is specific to uranium turnings that have been encapsulated in cement. Almost all of the waste contains depleted uranium (DU), but a very small fraction contains natural uranium and natural thorium. Contaminants will be identified through process knowledge and by sampling and analysis to demonstrate compliance with *Nevada Test Site Defense Waste Acceptance Criteria, Certification, and Transfer Requirements*, NVO-325 (Rev. 1).

This plan applies only to the encapsulated uranium turnings waste stream BCLA-HWMEU0006. The encapsulation process and the sampling for analysis will be carried out at Scientific Ecology Group, Inc. (SEG), 1560 Bear Creek Rd., Oak Ridge, Tennessee 37830. Details of this waste stream are discussed in the *Application to Ship Low-Level Radioactive Waste to the Nevada Test Site* (1).

This waste stream currently consists of 212 drums which potentially will be approved for processing. They contain machine turnings, grinding swarf, and fines that are primarily DU, stored under Trimsol machining coolant. Some of the drums have been in storage since 1984. Treatment consists of size reduction of the turnings by ring milling, followed by encapsulation in Type II Portland cement which is cast in split-form cylindrical molds. The final waste form is a monolithic solid that is chemically inert and contains no free liquids.

In May 1990, Nuclear Filter Technology, Incorporated (NFT) provided a waste characterization for 155 drums and sampled 26 representative drums. The analytical results were included in a report submitted in September 1990. The report revealed that 18 of the 26 drums should be classified as mixed waste (both hazardous and radioactive). The other 8 drums should be classified as strictly radioactive waste. The data received from NFT were neither conclusive nor sufficient to certify the waste as low-level radioactive waste; however, the data did indicate that the major source of potentially hazardous constituents is the liquid coolant. This led to the decision to decant the existing coolant and replace it prior to processing.

This preprocessing sampling will be done at LLNL prior to decanting of the Trimsol liquid, which will be segregated and disposed of separately (not at NTS) and is not part of this waste stream. As described below, the results of this preprocessing sampling will be used to determine which types of analyses must be performed on this waste stream in its final form. This preprocessing sampling will be done according to HWM Temporary Procedure TP-037, “Sampling and Analysis of D-38 Chips” (2). (This procedure does not have to meet the requirements of NVO-325 (Rev. 1) and is included here only for informational purposes.) This sampling will analyze both the sludge and the solid phases. Any excess liquid coolant will be removed.

After the Trimsol liquid has been removed, it will be replaced with new mineral oil, or another dispersant, and the drums will be repackaged and shipped to SEG for processing according to SEG Procedure STD-P-23-005, "Encapsulation of Depleted Uranium Turnings"(3). The process will consist of ring milling the turnings to achieve a uniform size and then adding them to the cement mixture. After mixing, the mixture will be poured into split-form molds that fit 55-gal drums.

Two to four drums will be batched for this processing. Because of this, and to ensure that there is an appropriate number of samples taken, drums will be selected randomly for sampling in their final waste form before any batching takes place, and only one drum selected for sampling will be allowed per batch.

Based on the results of this final waste form sampling, decisions will be made about whether or not the waste meets the requirements for disposal at NTS. Figure 1 is a flow diagram which illustrates the path that the waste will follow as it is processed, sampled, and analyzed. The analysis will be performed by Quanterra Environmental Services, 13715 Rider Trail North, Earth City, MO 63045. After processing, the material will be returned to LLNL before shipment to NTS or another approved disposal site.

As stated above, the current inventory of drums is 212. It is possible that additional drums in this waste stream will be generated very slowly and will be processed on an as-needed basis. Thus, while the bulk of this waste stream is currently legacy, it may develop into a continuous waste stream of very low volume. The current contract with SEG is for three years, but this may be renewed. Therefore, it is not realistic to create a timetable with specific milestones for this project.

1.2 Site Background

This plan is specific to the inventories of machine turnings generated at LLNL in B321C and to dust and particulates known as fines which are generated by the ISAM Program Facilities as part of the uranium refurbishment process described below. (The overwhelming majority of waste in this stream was generated at these two facilities. A very small proportion was generated at other LLNL locations.)

B321C is a machining facility known as the Special Materials Facility (it was formerly called the Numerical Control Facility). It is part of the Manufacturing and Materials Engineering Division of the Engineering Directorate. It is a general machine shop which services many areas of the Laboratory. The operations performed on the DU were turning and milling operations. Although other potentially hazardous metals such as beryllium, copper, and lead are machined in this shop, the DU machining is now done exclusively on dedicated machines, so that there can be no cross-contamination. Some of the drums go back to 1984 before this practice was

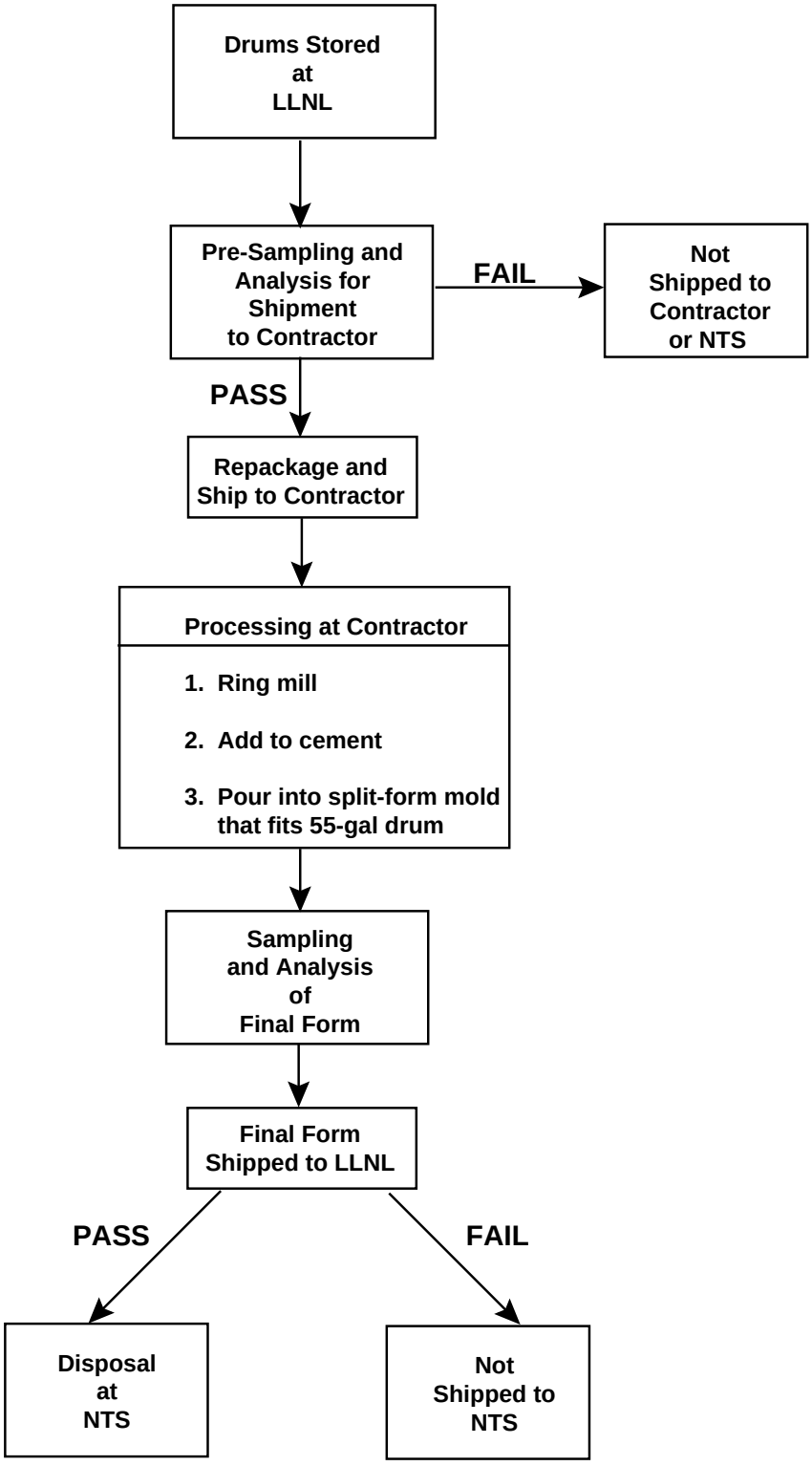


Figure 1. Plan for Processing, Sampling, and Analysis

instituted, but even during this time period, the machines were thoroughly cleaned before changing metals, and all the Trimsol coolant used for storing the chips was new.

The ISAM Facilities are part of the Uranium Atomic Vapor Laser Isotope Separation (U-AVLIS) Program, which has been developing a uranium isotope separation process since 1973. The process involves three major subsystems: lasers, separators, and uranium chemical processing for the interface with the nuclear fuel cycle. Lasers selectively charge the ^{235}U isotope in the separator where it is collected as enriched product. After removal from the separator, the product is chemically processed into a form acceptable as fuel for nuclear reactors.

The stage of the U-AVLIS process that relates to this waste stream is known as refurbishment. After a uranium demonstration run, all of the equipment that has been used is examined and cleaned. Sometimes this involves disassembly and reassembly of various components in preparation for the next run. This process generates fines containing uranium, which are swept or vacuumed up and stored in drums under Trimsol or water. The major part of these activities has been carried out in B175, but it can also occur in B490, B491, and B177.

2. PROJECT ORGANIZATION AND RESPONSIBILITIES

Several groups will be involved in the performance and review of this project. The Department of Energy, Nevada Operations Office (DOE/NV) will review and approve this plan as part of LLNL's application to ship the waste. SEG has the responsibility for processing and sampling the waste under the terms of its contract with LLNL. It also has the responsibility for shipping the samples to the analytical laboratory. The Environmental Protection Department's Hazardous Waste Management Division has the responsibility for pre-sampling and analysis, for repackaging the drums and shipping them to SEG, and for providing advice on the suitability of SEG procedures for sampling and training. The Waste Certification Program reviews SEG's training and procedures, validates data generated from sampling operations, and is responsible for ensuring that all the criteria described in NVO-325 (Rev. 1) are met prior to certifying the waste for final disposal. Overall authority for technical oversight of the SEG contract resides with the Environmental Process Engineering Group of the Environmental Protection Department's Hazardous Waste Management Division.

Functional project titles and responsibilities are:

The **HWM Waste Sampling Support Supervisor** (Susan Gagner) reviews all SEG procedures for sampling and training for sampling and advises on their suitability for use under this plan.

The **SEG Sampling Team Leader** (Billy Boyd) supervises the sampling team and assures that all applicable SEG and LLNL procedures are followed.

The **Environmental Process Engineering Group Leader** (John Bowers) has technical oversight of the SEG contract and overall responsibility for the processing, packaging, and transportation of the waste.

The **Waste Certification Engineer** (Blanca Haendler) reviews and validates all analytical data from sampling operations.

The **Waste Certification Program Manager** (Robert Fischer) assures that all SEG sampling operations comply with the requirements of this plan and NVO-325 (Rev. 1) and certifies that all applicable requirements for waste shipment are met. The WCPM also reviews SEG-supplied training and procedures.

A flowchart showing the sampling and analysis process and the persons and groups responsible for each step is shown in Figure 2.

3. COMPLIANCE WITH NEVADA TEST SITE WASTE ACCEPTANCE CRITERIA

The criteria set forth in *Nevada Test Site Defense Waste Acceptance Criteria, Certification, and Transfer Requirements,* NVO-325 (Rev. 1) that are relevant to this sampling and analysis plan are discussed in this section.

3.1 Transuranics

Not applicable: based on the known history of this waste stream, no transuranic radionuclides were machined at the facilities where these turnings were produced. The only expected radionuclides to be found are depleted uranium, natural uranium, and natural thorium.

3.2 Hazardous Materials

Low-level waste (LLW) to be disposed of at NTS cannot exhibit characteristics of, or be listed as, a hazardous waste as identified in Title 40, Code of Federal Regulations (CFR), Part 261 (RCRA) or under Title 22, California Code of Regulations (CCR). Therefore, analytical data must be provided to assure that no hazardous characteristics under these regulations are present within the waste prior to disposal at NTS. In order to ensure that this criterion is met, the samples will undergo the Waste Extraction Test (WET) procedure (sometimes referred to as the Soluble Threshold Limit Concentration [STLC] procedure) described in Appendix II of Section 66261 of Title 22. If the concentration of an extracted bioaccumulative or persistent toxic substance equals or exceeds that given as the STLC value pursuant to Title 22, the waste is hazardous. For inorganics, the WET (STLC) procedure has been chosen by LLNL for its Sampling and Analysis Plans over the Toxicity Characteristic Leaching Procedure (TCLP) referred to in NVO-325 (Rev. 1) because it will give additional metal constituents and is a more rigorous test. Comparison

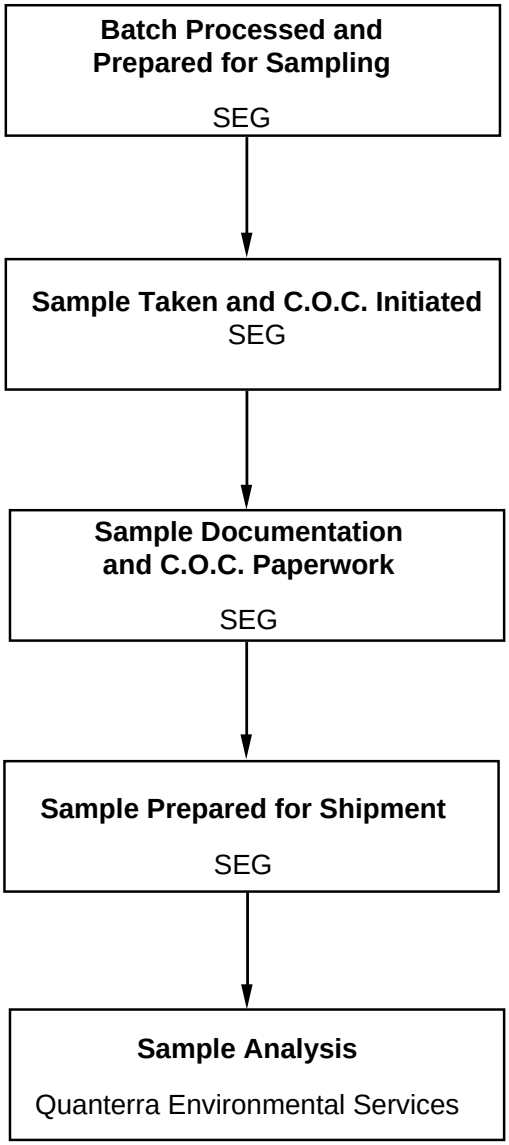


Figure 2. Responsibilities for Sampling and Analysis Process

data for these two procedures may be found in Ref. 4, which also contains a list of inorganic and organic persistent and bioaccumulative toxic substances and their STLC and Total Threshold Limit Concentration (TTLC) values.

Based on the specific knowledge of hazardous constituents contained in the liquids under which the turnings have been stored, the possibility of both inorganic and organic contaminants exists. The full suite of inorganics analyses, including mercury, will be performed by the WET procedure. Because of the difficulties anticipated in taking meaningful samples of volatiles and semivolatiles from curing cement, these analyses will be done only if the preprocessing sampling indicates that these contaminants may be present in the final waste form.

3.3 Free Liquids

LLW to be disposed of at NTS cannot contain any free liquids. Minor liquid residue that does not exceed 0.5% by volume of the external container is acceptable. Use of split-form molds in the encapsulation process allows a 100% visual inspection of the casting surfaces prior to packaging in shipping drums, which ensures that there are no free liquids present. Therefore, no analysis for free liquids will be performed.

3.4 Particulates

NVO-325 (Rev. 1) requires demonstration that the waste consists of no more than 1% by weight of particles less than 10 μm in diameter or 15% by weight of particles less than 200 μm in diameter. Encapsulation of the turnings in Portland cement will ensure that no particulates are present in this waste.

3.5 Gases

Radioactive gases and compressed gases (e.g., aerosol cans) as defined by 49 CFR 173.300 need to be stabilized or absorbed so that the pressure in the waste container does not exceed 1.5 atm at 20°C. These gases are not present in this waste stream. Based on this information, analysis to demonstrate compliance with this criterion is not required.

3.6 Stabilization

NVO-325 (Rev. 1) requires that waste be treated to reduce volume and provide a more physically and chemically stable waste form. Ring milling allows greater loadings of DU in each final waste form, which reduces overall disposal volume. Encapsulation of the turnings in Portland cement will create a stable waste form.

3.7 Etiologic Agents

LLW containing etiologic agents as defined in 49 CFR 173.386 will not be accepted for disposal at NTS. This waste stream does not contain these agents, so no analysis is required to demonstrate compliance with this criterion.

3.8 Chelating Agents

LLW containing chelating agents at concentrations exceeding 1% by weight will not be accepted at NTS. This waste stream is not contaminated with chelating agents, so no analysis is required to demonstrate compliance with this criterion.

3.9 Polychlorinated Biphenyls (PCBs)

PCB-contaminated LLW will not be accepted for disposal at NTS unless the PCB concentration meets municipal solid waste disposal levels of 50 ppm or less. California regulates PCBs in concentrations greater than 5 ppm, and this more rigorous standard is maintained by NTS for waste coming from California. Based on the known history of this waste stream, there is no reason to suspect that PCBs would be present. However, PCBs will be included in the preprocessing sampling of this waste stream (see Section 1.1). If evidence of PCBs is found, then this analysis will also be included in the sampling of the final waste form under this plan.

3.10 Explosives and Pyrophorics

LLW containing explosives and/or pyrophoric material in a form that may spontaneously explode or combust if the container is breached will not be accepted at NTS. Uranium is a known pyrophoric substance; however, the process of encapsulating the turnings in Portland cement will ensure that the uranium will not exhibit this property, because it will eliminate the possibility that the uranium could be exposed to air. Thus, analysis is not required to demonstrate compliance with this criterion.

4. QUALITY ASSURANCE OBJECTIVES

The quality assurance objectives of this plan are identical to those described in the previously approved "Sampling and Analysis Plan for Contaminated Soil," which is Appendix B of *Application to Ship Low-Level Radioactive Waste to the Nevada Test Site*. Specifically, the objectives are described in Section 4, subsections 4.1 Quality Assurance Objectives for Measurement; 4.2 Precision, Accuracy, Representivity, Comparability, Completeness (PARCC); 4.3 Audits; 4.4 Procedures; and 4.5 Sample Control. This section and its subsections are hereby incorporated by reference. For the complete citation, see Ref. 5. However, since in this case SEG will do the sampling according to its own procedures, the EAS procedures cited in this reference do not apply and will not be used (with the exception of EAS-107, which contains a discussion of method detection limits and is still a valid reference).

5. SAMPLING

5.1 Sampling Objectives

The objective of the sampling effort is to verify generator knowledge of the encapsulated uranium turnings waste stream (BCLA-HWMEU0006) in order

to show compliance with NVO-325 (Rev. 1) and to provide legally defensible data for disposal of this waste to the NTS.

5.2 Sampling Frequency and Selection

As indicated above, the preprocessing sampling will test 100% of the drums. Based on the results of this sampling, drums containing hazardous constituents above the applicable regulatory limits will be segregated as mixed waste. The remaining drums will constitute the population that is eligible for sampling and analysis under this plan. The selection of drums for this sampling will be by simple random sampling based on a calculation using the preprocessing sampling results and Equation (8) of SW-846 (6). If the result of this calculation is less than 10% of the total number of eligible drums, then 10% of the drums will be selected for sampling.

The selection of drums for sampling will be done before any batching or processing is carried out, and only one selected drum will be allowed per batch. Since the batch will be thoroughly mixed in a cement-type mixer prior to sampling, it can be assumed to be homogeneous, and only one grab sample will be taken per batch. Selection of a drum for sampling will be noted on the parcel card and on the Uranium Repackaging Certification Checklist.

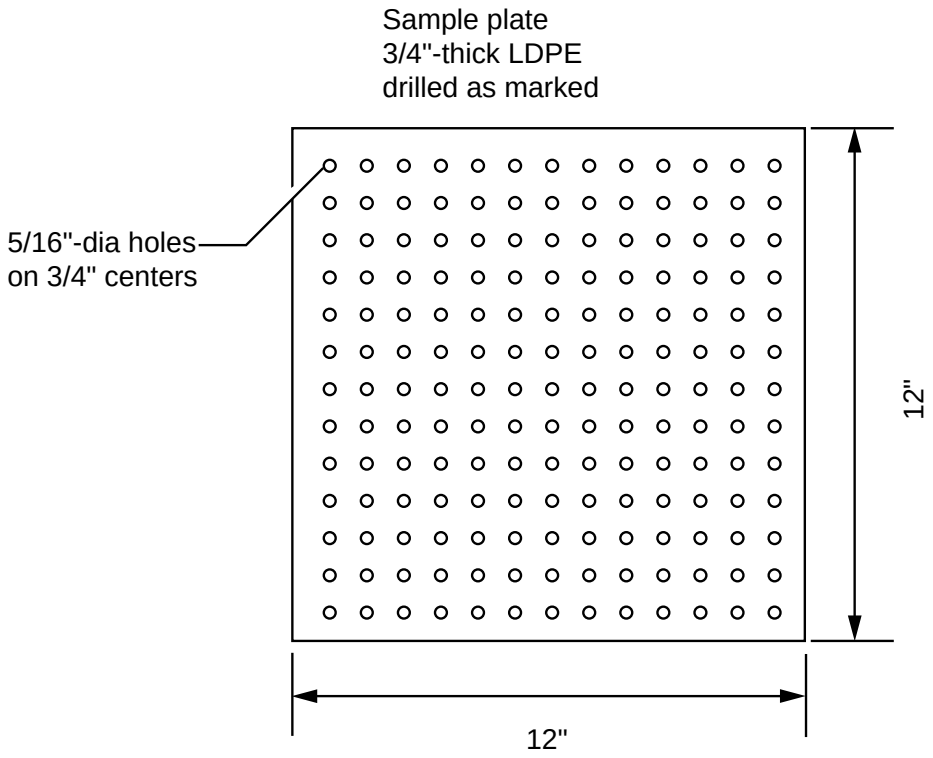
5.3 Sampling Strategy

Sampling shall be conducted with consideration to collecting representative samples, minimizing cross-contamination, and minimizing exposure to as-low-as-reasonably-achievable (ALARA) levels.

5.4 Sampling Methodology

Sampling of the encapsulated uranium turnings will be done in accordance with Ref. 3. (The relevant part of this procedure is reproduced in Appendix 1.)

The procedure calls for spreading a portion of the wet cement mixture containing the uranium turnings onto a specially designed low-density polyethylene (LDPE) or other chemically inert mold containing 169 cylindrical holes that are 5/16 in. in diameter and 3/4 in. deep (see Figure 3). This will be done so that the mixture is forced into the cylindrical holes with a trowel. Any large pieces of uranium that remain on the surface of the mold will be removed and returned to one of the split-form molds into which the batch was processed. The mold will be placed in a controlled access area until the cement has completely set. The cylindrical plugs will be removed and consolidated as the analytical samples. (At the analytical laboratory, the samples will be ground to meet the requirement of 2-mm-diameter particles for the STLC test.) A calculation has been done which indicates that each mold will produce a sufficient weight of cylindrical plugs to supply to the analytical laboratory for the STLC test. It is important to note that since the samples cannot be removed from the mold until the cement is set, the point of sampling is defined as the point at which these cylindrical plugs are



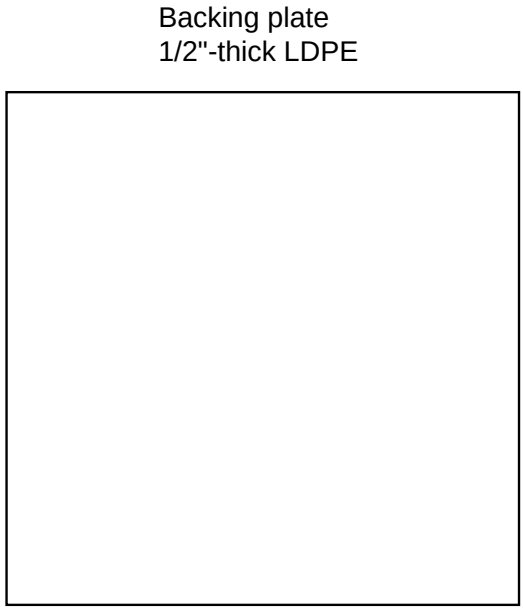


Figure 3. Schematic Diagram of LDPE Sampling Mold

removed. However, in order to ensure that the intent of hold time requirements is not defeated, the sampling procedure states that the plugs must be removed from the mold within 18 h of the time the cement is set (cure time is 12 h).

All samples will be logged and tracked in accordance with SEG Procedure RL-ADM-A-100, "Radioanalytical Laboratory Administrative Program" (7), SEG Procedure RL-RAM-I-101, "Sample Receipt and Log-in"(8), and SEG Procedure OP-6.9, "Chain-of-Custody" (9). Because NVO-325 (Rev. 1) requires the use of chain-of-custody seals, the SEG Sampling Team Leader will ensure that those seals are used and will record this fact in the "Comments" section of the Chain-of-Custody Form.

6. WASTE ANALYSIS SUMMARY

The waste analysis to be performed shall be conducted in accordance with NVO-325 (Rev. 1) and the methods referenced therein and in accordance with Ref. 6 as follows:

- Inorganics Analysis. The metals will be extracted by the WET procedure (CCR Title 22, Section 66261**,** Appendices I and II) and analyzed for soluble metals (STLC), including mercury.
- Organics Analysis. If necessary (see Section 3.2), volatile organic contaminants will be extracted using a TCLP zero head space extractor (ZHE) and analyzed using EPA SW-846 Method 8240. If necessary, semivolatile organics will be analyzed by EPA SW-846 Method 8270A after a TCLP extraction. If necessary (see Section 3.9), PCBs will be analyzed by EPA Method 8080.
- Radiological Analysis. This will include gamma and alpha spectroscopy. Target isotopes will be ^{234}U, ^{235}U, and ^{238}U; ^{230}Th and ^{232}Th; ^{238}Pu and ^{239}Pu; and ^{241}Am.

7. DATA INTERPRETATION

If none of the resulting hazardous analyte concentrations equals or exceeds the regulatory threshold for that substance, the samples taken can be considered to be an adequate demonstration that the waste in the containers as represented by these analytical data are non-hazardous and, therefore, radioactive waste. If one or more concentrations equal or exceed the regulatory threshold, we are faced with the question of whether the contamination is: localized with respect to that particular container; localized with respect to all of the containers; or general, requiring analysis of each container. However, in this case, a particular problem arises because the remaining batches will already have been processed by the time these data are available. Therefore, in order to allow for sampling of additional batches, all batches will be sampled into molds at the time of processing and the molds preserved in a properly maintained and logged refrigerator until the

analytical data are available. These samples can then be used for additional analysis if required. These samples will be shipped to LLNL for archiving. The storage of these samples will be the responsibility of the EAS laboratory. (Note: this approach will only work for STLC metals with the exception of mercury. In other cases, the hold times will almost certainly have been exceeded by the time the analytical results are available.)

Using the principle of simple random sampling, the following sampling criteria will be used:

> Concentration(s) of RCRA-hazardous or CA-regulated analyte(s) equaling or exceeding its (their) respective regulatory threshold in any batch will cause the analysis of an additional 10% of the total number of drums using the samples previously stored and preserved. If this resampling shows any sample with concentration(s) of RCRA-hazardous or CA-regulated analyte(s) equaling or exceeding its (their) respective regulatory threshold, then the entire population of processed drums will be segregated and not sent to NTS for disposal. Alternately, LLNL may opt to have each previously stored and preserved sample analyzed and segregate the waste stream on a drum-by-drum basis.

8. REFERENCES

1. *Application to Ship Low-Level Radioactive Waste to the Nevada Test Site*, Addendum #5, Section III, p. 5-3, Lawrence Livermore National Laboratory, UCRL-CR-111746 (latest revision), 1995.

2. HWM Temporary Procedure TP-037, "Sampling and Analysis of D-38 Chips," Lawrence Livermore National Laboratory, latest revision.

3. SEG Procedure STD-P-23-005, "Encapsulation of Depleted Uranium Turnings," Scientific Ecology Group, latest revision.

4. *Application to Ship Low-Level Radioactive Waste to the Nevada Test Site*, Appendix B, Sub-Appendix A-1, pp. 16-24 and G-2 - G-15, Lawrence Livermore National Laboratory, UCRL-CR-111746 (rev. 1), 1993.

5. *Application to Ship Low-Level Radioactive Waste to the Nevada Test Site*, Appendix B, Section 4, pp. 17-22, Lawrence Livermore National Laboratory, UCRL-CR-111746 (rev. 1), 1993.

6. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, (latest edition), U. S. Environmental Protection Agency.

7. SEG Procedure RL-ADM-A-100, "Radioanalytical Laboratory Administrative Program," Scientific Ecology Group, latest revision.

8. SEG Procedure RL-RAM-I-101, “Sample Receipt and Log-in,” Scientific Ecology Group, latest revision.

9. SEG Procedure OP-6.9, “Chain-of-Custody,” Scientific Ecology Group, latest revision.

APPENDIX 1

ENCAPSULATED TURNINGS SAMPLING PROCEDURE*

Wastes consisting of encapsulated uranium turnings (NTS Waste Stream Number BCLA-HWMEU0006) shall be sampled using the following procedure:

- From each batch of cement after thorough mixing, take one grab sampling with a plastic cup 16 oz in size.
- Using a stainless steel spatula or other flat-bladed tool, spread the contents of the cup over the LDPE sampling mold so that all the cylindrical holes are filled as uniformly as possible. Large chunks of material which will not enter the holes should be removed and returned to one of the split-form molds into which the batch was poured.
- Place the sampling mold in a secure, access-controlled location and allow to cure for 12 h.
- Within 18 h of the time the cement in the mold is cured, invert the mold and tap out the cylindrical pellets of sample. Composite the pellets in sampling jars.
- For each group of 10 samples, one random field duplicate will be obtained by taking an additional grab sample from one of the batches. In addition, a sample of distilled water will be used as a trip blank, and for each group of 20 samples a batch of clean cement will be prepared and sampled as a field blank.

Note: Each sampling mold will be used only once, so there is no need for a decontamination procedure for the molds. Each mold will be cleaned prior to use by a procedure adapted from EAS-307, “Decontamination of Sampling Equipment.”

*The important sampling steps have been reproduced here from Ref. 3 as a convenience to the reader. In case of any discrepancies between this document and Ref. 3, the SEG procedure is the controlling document.

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